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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

No. 1164

THE SYNTHESIS AND PURIFICATION OF AROMATIC HYDROCARBONS

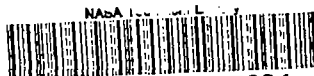
V - 1-ETHYL-3-METHYLBENZENE

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SUMMARY

The method used for the synthesis and purification of an 8-gallon quantity of 1-ethyl-3-methylbenzene from m-cresol consists in obtaining m-methylcyclohexanone from m-cresol by hydrogenation followed by oxidation, condensation of the ketone with ethylmagnesium bromide, dehydration of the tertiary alcohol obtained, and dehydrogenation of the olefins to 1-ethyl-3-methylbenzene. A yield of 28 percent of the theoretical was obtained from 98 percent commercial m-cresol. The physical properties of 1-ethyl-3-methylbenzene are compared with selected values from the literature.

INTRODUCTION

The synthesis and purification of 1-ethyl-3-methylbenzene was undertaken at the NACA Cleveland laboratory in conjunction with the study of aromatic hydrocarbons as possible components of aviation gasoline. Previously reported are results on the preparation of butylbenzene (reference 1), 1,2,4-trimethylbenzene (reference 2), isobutylbenzene, sec-butylbenzene, tert-butylbenzene (reference 3), and 1,2,3-trimethylbenzene (reference 4).

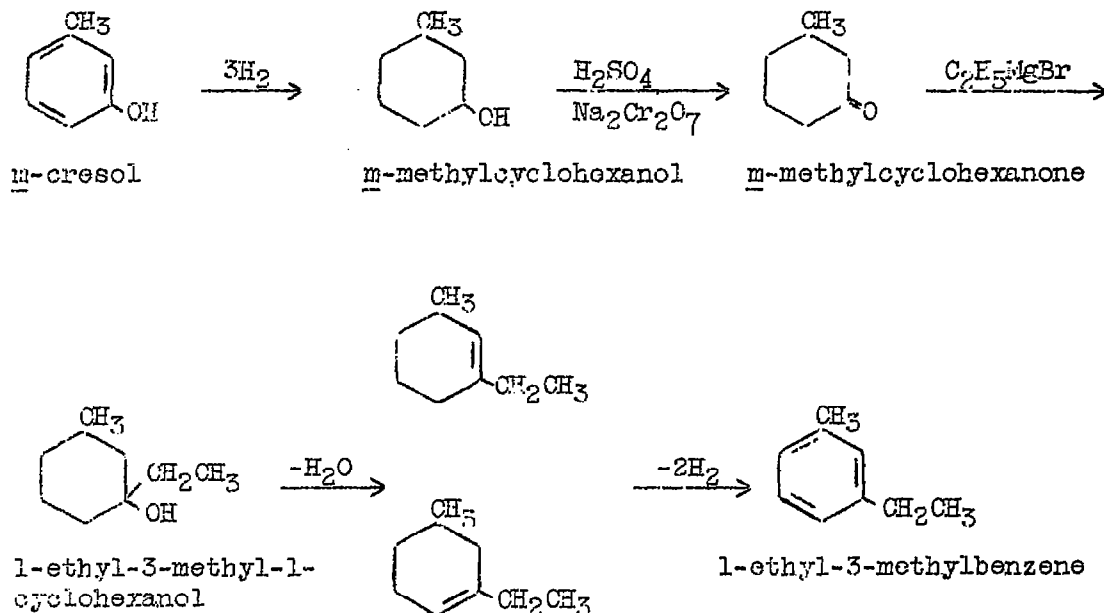
Only two of the methods reported in the literature for the synthesis of 1-ethyl-3-methylbenzene were considered adaptable to large-scale preparation of this hydrocarbon. Wroblevsky (reference 5) prepared 1-ethyl-3-methylbenzene by converting m-toluidine to m-bromotoluene, which was subsequently treated with ethyl bromide and metallic sodium. The hydrocarbon was prepared by von Auwers (reference 6) from m-tolualdehyde. Methylmagnesium halide was condensed with m-tolualdehyde to give methyl tolyl carbinol, which was

then converted to m-methyl acetophenone and reduced to 1-ethyl-3-methylbenzene. The foregoing methods appeared less readily adaptable to large-scale synthesis of the hydrocarbon than the method used in the present synthesis.

The synthesis and purification of an 8-gallon quantity of 1-ethyl-3-methylbenzene, using m-cresol as starting material, is described and the physical properties are given.

DISCUSSION OF SYNTHESIS

The method of synthesis may be summarized schematically as follows:



Commercial m-cresol (98 percent) was hydrogenated quantitatively to m-methylcyclohexanol. Oxidation of the alcohol by the method described in reference 7 gave fair yields of m-methylcyclohexanone. Analysis of the oxidation product for m-methylcyclohexanol by the acetylation method described in reference 8 indicated that the product contained approximately 20 percent unconverted m-methylcyclohexanol. An attempt to purify the m-methylcyclohexanone by fractional distillation at atmospheric pressure led to intermolecular dehydration of two

moles of the ketone. Therefore, ethylmagnesium bromide was prepared in excess and the crude m-methylcyclohexanone was added without purification. The unchanged m-methylcyclohexanol from the oxidation reaction was dehydrated along with the tertiary alcohol obtained from condensation of the ketone with ethylmagnesium bromide, and the resulting olefins were separated by fractional distillation. A single distillation of the crude 1-ethyl-3-methylcyclohexenes through a modified Fenske column of 40-theoretical plates gave the distillation and refractive-index curves shown in figure 1. The constant-index material from this distillation was dehydrogenated to 1-ethyl-3-methylbenzene.

The crude product of dehydrogenation was distilled through a 2-inch by 26-foot stainless-steel modified Fenske column of 100-theoretical plates. The distillation and refractive-index curves for 1-ethyl-3-methylbenzene are given in figure 2. Constant-index material from the first distillation was combined and refluxed over sodium to remove the last traces of the colored impurities present. The hydrocarbon was again distilled through a 100-theoretical plate column. The physical constants for the 1-ethyl-3-methylbenzene together with values from other sources are as follows:

Compound	Source of constants	Melting point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (grams/ml)
1-Ethyl-3-methylbenzene	Cleveland laboratory	-95.62	161.3	1.4965	0.8644
	Reference 9	-----	161.5-162.5	^a 1.498	^a .8690
	Reference 10	^b -95.55	161.3	1.4965	.8646

^aAt 17.9° C.

^bFreezing point.

The melting curve for the best sample of 1-ethyl-3-methylbenzene obtained at the Cleveland laboratory is shown in figure 3. The hydrocarbon supercooled to such an extent that no equilibrium freezing curves could be obtained.

The over-all yield of 1-ethyl-3-methylbenzene was 28 percent of the theoretical when commercial m-cresol (98 percent) was used as starting material.

EXPERIMENTAL DETAILS

An 8-gallon quantity of 1-ethyl-3-methylbenzene was prepared according to the reactions previously outlined. Typical quantities of the reactants and yields of the products are given in the following discussion.

Hydrogenation of m-cresol. - In a typical hydrogenation run, 10.4 kilograms (96.5 moles) of m-cresol and 250 grams (2.5 percent by weight) of catalyst (nickel on kieselguhr) were placed in a 20-liter hydrogenation bomb. Hydrogenation was carried out at a temperature of 160° C and at a maximum pressure of 1800 pounds per square inch. Each time the pressure in the bomb fell below 100 pounds per square inch additional hydrogen was added. Approximately 12 hours were required to complete the hydrogenation. The theoretical yield of m-methylcyclohexanol was obtained.

Oxidation of m-methylcyclohexanol. - Approximately 35 gallons of water, 14.1 liters of concentrated sulfuric acid (specific gravity 1.84), and 31.7 kilograms of sodium dichromate were mixed with stirring in a 100-gallon glass-lined reactor. The mixture was heated to 55° to 60° C and then 17.2 kilograms (150 moles) of m-methylcyclohexanol was slowly added from a large separatory funnel over a period of 3 hours. After addition of the alcohol was completed, the mixture was stirred for 15 hours at 50° to 60° C and then steam distilled. The crude m-methylcyclohexanone (10.6 kg or 62 percent of the theoretical yield) was analyzed for unconverted m-methylcyclohexanol by the acetylation method of Shaefer (reference 8). Approximately 20 percent of the crude material was found to be unconverted m-methylcyclohexanol. On the assumption that the remaining 80 percent of the crude material was m-methylcyclohexanone, a yield of 50 percent of the theoretical was obtained.

Preparation of 1-ethyl-3-methyl-1-cyclohexanol. - Ethylmagnesium bromide was prepared in a 100-gallon glass-lined reactor from 10 kilograms (410 moles) of magnesium turnings and 46.4 kilograms (425 moles) of ethyl bromide in 25 gallons of ethyl ether. Approximately 6 hours were required for addition of the ethyl bromide and the mixture was stirred over night.

The crude m-methylcyclohexanone was dried over alumina and used without further purification. To the ethylmagnesium bromide, prepared in excess, 31.8 kilograms (284 moles) of the crude m-methylcyclohexanone in 10 gallons of ether was slowly added from the large separatory funnel over a period of 6 hours. The mixture was stirred over night and then hydrolyzed with dilute hydrochloric acid. The ether

layer was washed once with a saturated solution of sodium bicarbonate and twice with water. The ether was distilled from the mixture and the residual oil distilled under reduced pressure. The material (31.8 kg) distilling between 95° and 120° C at 50 millimeters was collected as crude 1-ethyl-3-methyl-1-cyclohexanol.

Dehydration of the alcohol. - The crude 1-ethyl-3-methyl-1-cyclohexanol (31.8 kg) was dehydrated at 250° to 270° C by one pass through a 2-inch by 10-foot column packed with alumina. Both the 1-ethyl-3-methyl-1-cyclohexanol and the m-methylcyclohexanol, carried through from the oxidation reaction, dehydrated at this temperature to give 27.5 kilograms of unsaturated hydrocarbon. The dehydration of the alcohols was quantitative with only a 3-percent mechanical loss in total recovery. The mixed olefins were distilled through a modified Fenske column of 40-theoretical plates. Approximately 20 percent of the unsaturated hydrocarbon was methylcyclohexene. This amount of methylcyclohexene agrees well with the 20-percent m-methylcyclohexanol found by analysis of the crude m-methylcyclohexanone obtained from the oxidation reaction. After fractionation the yield of the isomeric 1-ethyl-3-methylcyclohexenes was 19.4 kilograms or 55 percent of the theoretical based on the crude m-methylcyclohexanone as the limiting factor.

Dehydrogenation of the 1-ethyl-3-methylcyclohexenes. - The purified 1-ethyl-3-methylcyclohexenes (19.2 kg or 155 moles) were dehydrogenated at 460° to 470° C by one pass through a 2-inch by 10-foot column packed with chrome-alumina catalyst. The product from the dehydrogenation was fractionated once through a 100-theoretical plate column. The material (15.3 kg) that distilled between 160° and 161° C was combined and refluxed over sodium to remove traces of colored impurities and was then redistilled. The yield of 1-ethyl-3-methylbenzene on dehydrogenation was 82.5 percent of the theoretical based on the purified 1-ethyl-3-methylcyclohexenes.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, May 15, 1946.

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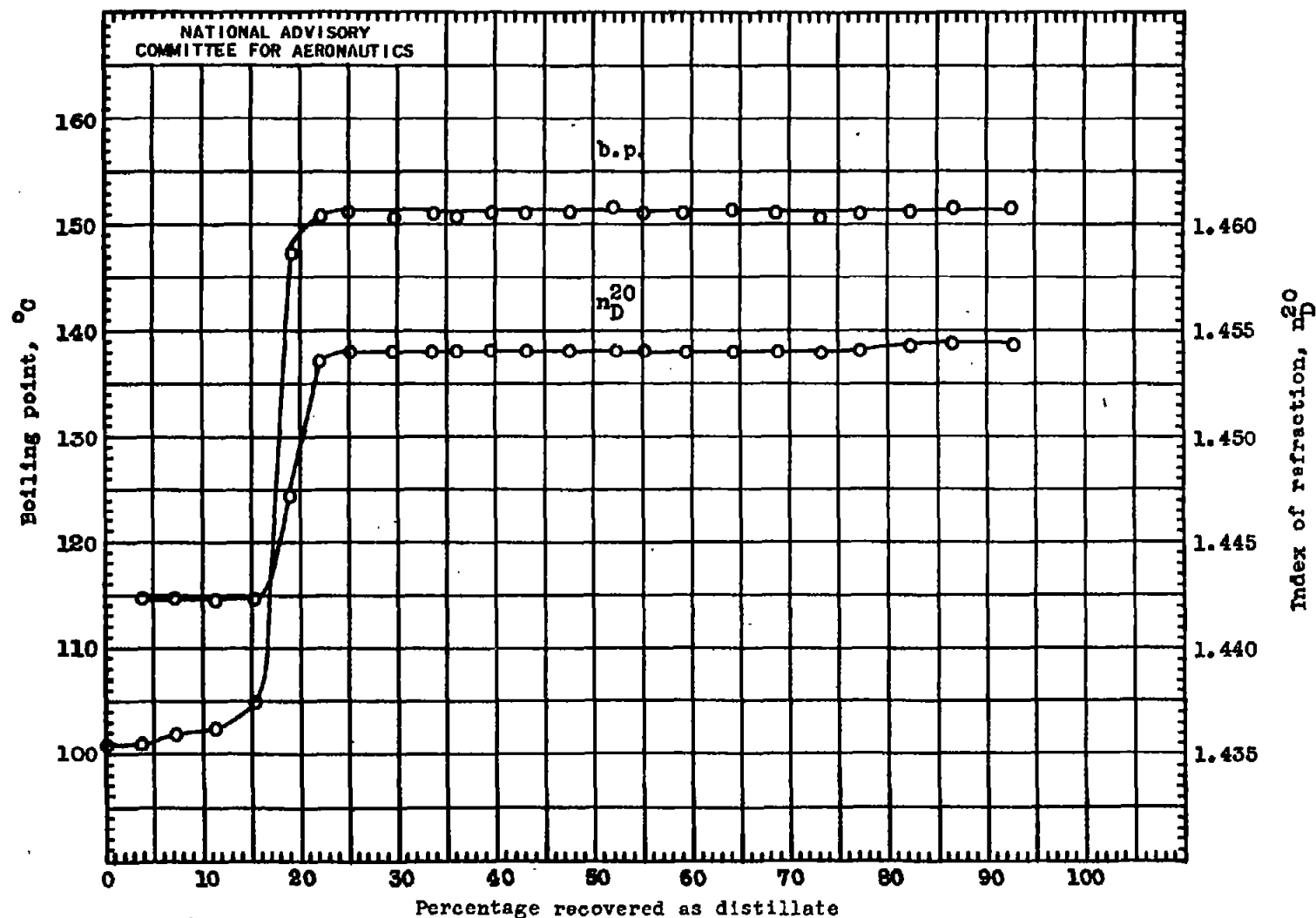


Figure 1. - Variation of boiling point and index of refraction with percentage recovered as distillate for 1-ethyl-3-methylcyclohexenes.

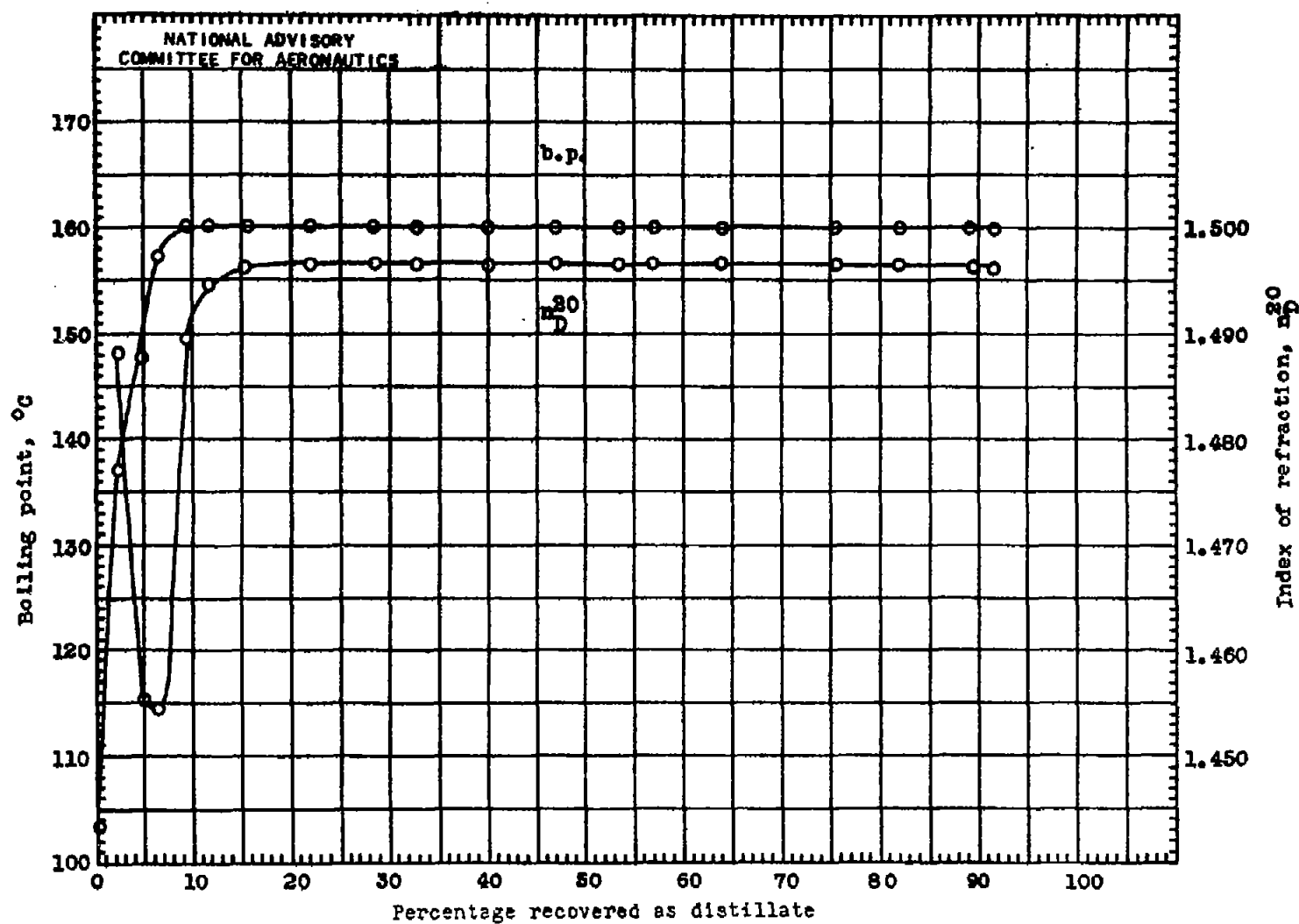


Figure 2. - Variation of boiling point and index of refraction with percentage recovered as distillate for 1-ethyl-3-methylbenzene.

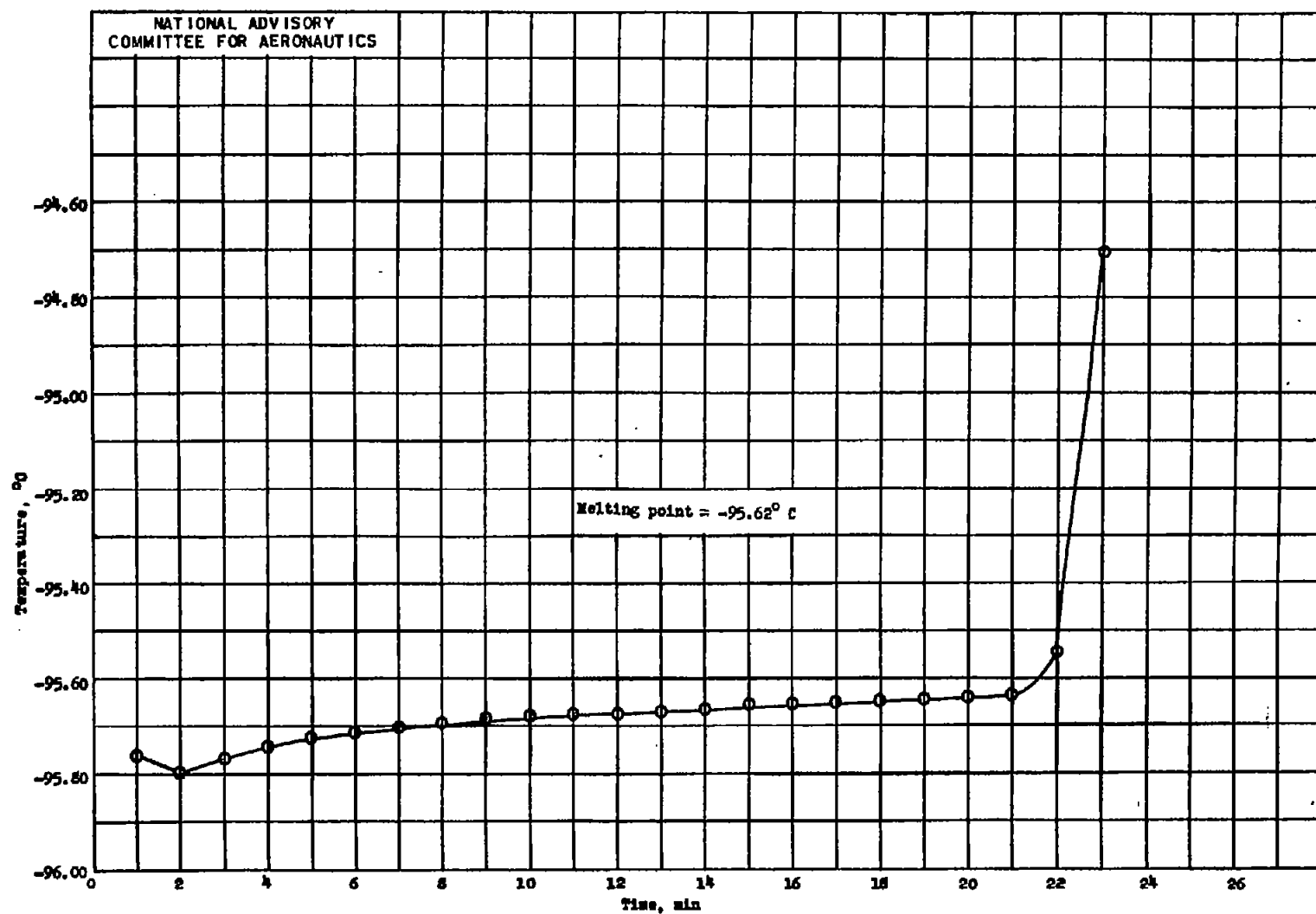


Figure 3. - Time-temperature melting curve of 1-ethyl-3-methylbenzene.